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STUDY OF REFRACTORY MATERIAL FOR USE IN A SLAGGING COAL GASIFER

by

George F. Dickey

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The atmosphere and the slagging conditions that exist in slagging a fixed-bed Lurgi-type coal gasifier requires dense high-alumina-type refractories that are low in iron and silica. To resist the slags that are formed, the dense high-alumina-type refractories are needed to obtain a feasible life, as a result of the corrosion and erosion. The use of water-cooling coils to cool the refractory material could result in a catastrophe in the event of a leak.

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PREFACE

The work described in this report was authorized under Project BA-07-04, Task 6, Trade-off Studies of Refractory Materials for Use in Slagging Coal Gasifiers. The work was started in October 1976 and completed in April 1977.

The information in this document has not been cleared for release to the general public.

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STUDY OF REFRACTORY MATERIAL FOR USE IN A SLAGGING COAL GASIFIER

I. INTRODUCTION.

The Energy Research and Development Administration (ERDA)* is contracting for the design, construction, and operation of coal gasification demonstration plants for the production of clean (sulfur-free) high-Btu fuels. Many of the coals contain significant quantities of trace materials which are expected to be particularly corrosive and erosive to the ceramics used as refractory materials in the coal gasifier proposed in the various coal conversion demonstration plant processes.[1] In support of these programs, a study of refractory materials available for use in two candidate coal gasification systems was made as provided for in the Memorandum of Understanding (MOU) between the ERDA and the Army Development and Readiness Command (formerly Army Materiel Command), E (49-18) 2221, dated 16 September 1975.[1]

Within the time frame of current demonstration plant programs, it is necessary to apply the experience and knowledge that presently exist concerning refractory materials and designs. The study was limited to the various types of refractory material that would be suitable for use in the slagging-type coal gasifiers. Two slagging-type coal gasifiers were considered: the slagging-fixed-bed (Lurgi) gasifier and the entrained/slagging (Bi-gas) gasifier.

The purpose of this investigation was (1) to determine the industrial experience in refractories related to specific coal conversion processes, and (2) to make recommendations for application of this experience for proposed demonstration plants. Information for the investigation was obtained from literature searches and, most importantly, from direct discussions with industrial users and suppliers of refractories. The study emphasized refractory experiences applicable to the slagging-fixed-bed gasifier and the Bi-gas entrained bed gasifier. Both gasifiers operate at high temperatures (approximately 2600° to 3000°F) under pressure. Gasifiers operating at a lower temperature in the nonslagging mode involve conditions that are less harsh.

II. STATEMENT OF THE PROBLEM.

A. Gasifier Systems.

In the slagging-fixed-bed gasifier and the Bi-gas gasifier there appear to be problems concerning the corrosion/erosion of the refractory material, especially in the slagging areas. When one reviews the construction of the Bi-gas as to refractories and those proposed for the fixed-bed slagging gasifier, a great many differences are found in the reactor design that affect its operation, especially startup and shutdown procedures and other factors that impact upon the selection of refractory materials. The various operating factors, such as pressure and temperature, influence the design of the reactor as well. The refractory material to be used is normally selected early in the design, soon after the process parameters are known, so that the needed refractory engineering consideration can be incorporated. Some of the main considerations of the process that affect the selection of refractories used are the feedstock (coal), operating conditions such as pressure, temperature, produced gases, gas velocity, and the slag formed (fluidity).

*Now the Department of Energy (DoE).

1. Slagging-Fixed-Bed Gasifier.

Development of the slagging-fixed-bed gasifier is spearheaded by the ERDA-CONOCO* project to design, build, and operate a pipeline gas demonstration plant.[1,2] The demonstration plant is based on design criteria to convert approximately 3900 tons/day (T/D) of high-sulfur, bituminous, caking coal to approximately 59 million ft^3 of pipeline gas with a heating value of 955 $Btu/stdft^3$. The process is expected to produce approximately 500 T/D of slag (depending upon the coal). The process was developed by British Gas, Inc., at the Westfield Development Center, Scotland.

The operation conditions of the gasifier will be the utilization of high pressure (approximately 450 psig) and high temperature (~ 2800°F), especially in the slagging or combustion zone of the furnace. The fixed bed is a moving burden similar to that found in blast furnace operations with the gaseous products moving countercurrent to the bed and the slag running down walls and collecting in the hearth.[3] The area of slag formation and removal provides a severe environment for refractories.

2. Entrained Bed Gasifier.

The Bi-gas gasifier is a two-staged, high-pressure, oxygen-steam, entrained (coal) flow gasifier. The 120 T/D pilot plant at Homer City, PA, for the Bi-gas process is scheduled to be operational in 1977. The Bi-gas reactor is divided into two stages. In stage I (lower stage), the gasification consists of a vortex flow char - O_2 - steam at approximately 2700°F and at a pressure of 1000 psig. The slag from the coal char runs from the hearth and is quenched in water while the product gases rise into stage II (upper stage). The temperature of the gases in stage II is approximately 1700°F and the pressure is approximately 1000 psi. In stage II, raw coal and steam are the reactants and the formed char is recycled to stage I.

B. Coal Feedstock.

Both the slagging, fixed-bed gasifier and the entrainment Bi-gas gasifier should be capable of processing a variety of feedstocks producing a synthetic natural gas product and slag. Table 1 lists a typical analysis of the coal to be found in the United States. Table 2 is an analysis of an Ohio coal, Meigs No. 9. It should be noted that the sulfur content of this eastern coal is approximately 5%, and that the coal contains pyritic as well as organic sulfur. The Meigs No. 9 is a candidate coal in the ERDA-CONOCO* Demonstration Plant Project. The ash analysis is of primary importance in refractory considerations and is presented as a basis for later discussions.

C. Gaseous Environment.

As the coal is being reacted with steam and/or oxygen, gaseous products are being formed. The common gases are identified as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4), and other hydrocarbons. To establish the resistance of various refractories to these gaseous products the pilot plants HYGAS, CONSOL, SYNTHANE, BATTELLE, and BCR are participating in a program to evaluate various commercial refractories.[4] The various gaseous constituents affect refractories in differing ways.

* Conoco Coal Development Company.

Table 1. Typical Analysis of United States Coals*

Fuel classification	Locality	Moisture	Analysis on dry basis								Btu value MAF
			Proximate			Ultimate					
			VM	FC	Ash	S	H_2	C	N_2	O_2	
Lignite	North Dakota	36.0	50	38	12	1.8	4.0	64.7	1.9	15.5	11,038
Sub-bituminous C	Wyoming	22.3	40	45	15	3.4	4.1	61.7	1.3	14.6	10,598
Sub-bituminous A	Wyoming	12.8	39	55	6	0.4	5.2	73.1	0.9	14.6	12,902
Hi-bituminous B	Illinois	8.6	35	56	9	1.8	4.8	74.6	1.5	8.9	13,388
Hi-bituminous A	Pennsylvania	1.4	34	59	7	1.3	5.2	79.5	1.4	6.1	14,396
Bituminous volatile	West Virginia	3.6	16	79	5	0.8	4.8	85.4	1.5	2.6	15,000
Bituminous (Pittsburgh)	West Virginia	2.5	39	54	7	2.3	5.0	75.0	1.5	6.7	13,000
Bituminous	Ohio	3.6	42	49	9	4.0	5.7	80.9	1.4	7.4	14,730

* Combustion Engineering, Inc., Published 1966.

NOTE: VM - volatile matter
FC - fixed carbon
MAF - moisture ash-free

Table 2. Analysis of Meigs No. 9 Seam (Ohio)*

Proximate analysis (as received)		Ultimate analysis (as received)		Forms of sulfur (as received)	
Moisture	8.0%	Carbon	56.3%	Pyritic	2.7%
Ash	18.9%	Hydrogen	5.0%	Sulfate	0.1%
Volatile matter	32.5%	Nitrogen	0.8%	Organic	2.3%
Fixed carbon	40.6%	Sulfur	5.1%		
		Oxygen	13.9%		
		Ash	18.9%		

* Coal analysis from Ohio Power Company, Muskingum River Plant, Ohio.

Hydrogen sulfide and sulfur dioxide are not considered particularly corrosive/erosive to refractory material. Hydrogen sulfide and sulfur dioxide can penetrate porous refractory materials and condense where they will be corrosive to the metal anchors in the lining and the reactor shell.[5,6]

Steam, hydrogen, and CO_2 have been suspects in damaging refractories, with steam being a most aggressive agent. Typical refractory corrosion by high-temperature steam involves the formation of silica acids from aluminosilicates as well as the extraction of any soluble oxides during startup or shutdown. Hydrogen will attack the silica-containing refractories at low pressures while steam reacts more rapidly at the higher pressures and temperatures. Carbon dioxide and carbon monoxide can react with some of the ceramics.[5,7,8]

Another mechanism of failure of refractories is noted from blast furnace experiences in carbon monoxide disintegration of refractories. This mechanism occurs at relatively low temperatures and it occurs because of the catalytic reduction of CO to C in the presence of iron or iron oxide.[6,7,9] Therefore, it is important that the iron content in refractories be minimal and that the refractory be fired, if possible, to tie up the iron as an iron silicate. Carbon monoxide disintegration can be prevented; therefore, it is not considered a major problem.[7]

Trace alkalies in the feedstock were considered a possible cause for the deterioration of refractory use in coal gasifiers.[9,10] This was based primarily on Dr. R. B. Snow's article.[9] When considering the slagging-fixed-bed gasifier, the descending burden carries a nominal potassium oxide (K_2O) and sodium oxide (Na_2O) content and the ascending gases may carry some potassium (K) and sodium (Na) vapors that are reoxidized so that little or no K or Na leaves with the gas stream. Almost all Na and K leave with the slag, although some may wet the refractory walls. This phenomenon is not considered to be detrimental provided a nonsilicate refractory is utilized. If a refractory containing silicates is used, the formation of alkali silicate can result in a breakup of the refractory. This is known as "alkali bursting" and is referred to in an article by Bakker and Crowley.[5]

The temperature effects on vapors and gases in contact with the refractory material are important. The furnace atmosphere will contain quantities of acids such as SO_2, hydrochloric acid (HCl), etc.; and when these acid gases penetrate the refractory wall and the temperature drops, these acids will condense. As a result, the corrosion problem may become severe. The same

consideration applies to the alkali compounds that are formed. The alkali compounds and the acids may reduce the action of each other to such a point that no real problem exists. If the hot-wall refractory material is not porous, it seems reasonable to assume that the problem will not exist and that the alkali and acidic compounds will be active only within or on the hot wall of the reactor. (Long-range effects will be observed in the demonstration plants.)

The use of a reducing atmosphere within the reactor introduces a problem not evident in many present-day boiler applications of refractories. As stated previously, the reducing gas, hydrogen, will attack silica-containing refractories at low pressure. Therefore, if highly reducing coal gasifiers are to be used, silica-containing refractories should be avoided. Carbon monoxide will react with the available iron; therefore, ceramics should be fired so that the free iron is not available to react.

D. Slag Environment.

The slag formed in the slagging gasifiers is very corrosive and erosive. The mechanical and thermal conditions favor a continuous fluxing and erosion of the refractory. As a result, one should expect the wearing away of the furnace's refractory lining. Many laboratory tests have been conducted in an effort to determine the resistance of various refractories to blast furnace and coal slags; however, laboratory tests do not necessarily predict actual practices. Dr. Koenig and his collaborators in West Germany developed a wear theory for refractories. With this theory, one assumes that no refractory is able to withstand the corrosive action of blast furnace (BF) slags and gases at high temperatures (>2750°F).[5,7] The residual thickness of the refractory lining in the bosh is dependent on the thermal conductivity of the refractory and the lowest temperature at which the refractory will react with any component with which the refractory is in contact. It is assumed that the slag/ash erosion and corrosion of refractories in a coal gasifier will be as complex as it is presently predicted in BF operations. Since the slag in a BF operation depends somewhat on the source of ore, it should be noted that the slag/ash from coals varies with every seam, and can even vary within a seam as to its composition and physical properties. This is evident in the bituminous coals used in the power generation plants; therefore, averages are used in determining the properties expected as to basicity and fluidity of slags formed in power-plant boilers.

The composition of typical coal ash and the related ash fusion temperatures of United States coals are shown in table 3. The analysis of the coal ash indicates what may be expected of some coal slags from various areas of the United States. As can be noted from table 3, the fluid temperature of coals can vary with the type of atmosphere in the gasifier (reducing or oxidizing) and the source of the coal used. To predict whether a slag would be fluid, studies were made to determine the relationship of the ash content of silica, iron, and dolomite on the viscosity of coal slags at various temperatures. These laboratory studies and field investigations supplemented investigations by the Bureau of Mines. The studies resulted in a method for calculating the temperature needed for maintaining a fluid coal slag for coals from the Eastern United States. It is obvious that coal slags formed in a gasifier should be fluid enough to flow into the quenching zones. One way to achieve fluidity is to add silica or dolomite. When visiting the Bi-gas pilot plant, we noticed that their process had allowed for the addition of these materials to the feed coal for the purpose of modifying the slag composition to obtain a fluid slag. A well-written article by Winegartner and Ubbens describes the melting properties, viscosity properties, and fouling potential of coals used in boiler plant operations.[11]

Table 3*. Ash Content and Ash Fusion Temperature of Some US Coals and Lignite

Rank	Low volatile bituminous	High volatile bituminous				Sub-bituminous	Lignite
Seam	Pocahontas No. 3	No. 9	Pittsburgh	No. 6			
Location	West Virginia	Ohio	West Virginia	Illinois	Utah	Wyoming	Texas
Ash, dry basis, %	12.3	14.10	10.87	17.36	6.6	6.6	12.8
Sulfur, dry basis, %	0.7	3.30	3.53	4.17	0.5	1.0	1.1
Analysis of ash, % by wt							
SiO_2	60.0	47.27	37.64	47.52	48.0	24.0	41.8
Al_2O_3	30.0	22.96	20.11	17.87	11.5	20.0	13.6
TiO_2	1.6	1.00	0.81	0.78	0.6	0.7	1.5
Fe_2O_3	4.0	22.81	29.28	20.13	7.0	11.0	6.6
CaO	0.6	1.30	4.25	5.75	25.0	26.0	17.6
MgO	0.6	0.85	1.25	1.02	4.0	4.0	2.5
Na_2O	0.5	0.28	0.80	0.36	1.2	0.2	0.6
K_2O	1.5	1.97	1.60	1.77	0.2	0.5	0.1
Total	98.8	98.44	95.74	95.20	97.5	86.4	84.3
Ash fusibility							
Initial deformation temperature, F							
Reducing	2900+	2030	2030	2000	2060	1990	1975
Oxidizing	2900+	2420	2265	2300	2120	2190	2070
Softening temperature, F							
Reducing		2450	2175	2160		2180	2130
Oxidizing		2605	2385	2430		2220	2190
Hemispherical temperature, F							
Reducing		2480	2225	2180	2140	2250	2150
Oxidizing		2620	2450	2450	2220	2240	2210
Fluid temperature, F							
Reducing		2620	2370	2320	2250	2290	2240
Oxidizing		2670	2540	2610	2460	2300	2290

* From Babcock and Wilcox's publication Steam/Its Generation and Use. 38th Ed. (1975).

The slag acid-to-base ratio is a suggested method for controlling the slag's fluidity thereby reducing the contact time of the slag on the refractory material within the furnace as well as an expeditious way to control slag removal from the gasifier. The ingredients of the slag can be classed as either basic or acidic. The basic constituents are ferric oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), and Na_2O; the acidic constituents are silicon dioxide(SiO_2), aluminum oxide (Al_2O_3), and titanium dioxide (TiO_2). The base-to-acid ratio of constituents can be used to predict the viscosity of the slag. As stated by Babcock and Wilcox,[12] the viscosity of a slag decreases as the base-to-acid ratio increases to one.

During the gasification of the coal, the fluid control of slags can be accomplished either by adding limestone or silica to the coal feed or by raising the temperature of the reaction zone within the furnace, or both. When controlling the fluidity of the slag by any one of the above-mentioned methods, the refractory material of the furnace must be able to resist the corrosion/erosion of the slag and its ingredients at the fluid temperature.

III. APPLICATION OF REFRACTORIES.

It is expedient that a slagging gasifier be lined with an ideal refractory. The ideal refractory should have the following properties:

1. Extremely high melting point (3000° to 3300°F).
2. Volume stable at operating temperatures.
3. Chemically stable—not affected by gases or slags.
4. Thermally stable—not affected by rapid temperature changes.
5. High load strength.
6. High density (low porosity).
7. Low thermal conductivity.
8. High abrasive resistance at elevated temperatures.

Of all refractory materials used today, none possess all the ideal properties. The fireclay refractories have only fair resistance to slags. The silica brick has fair resistance to chemical attack by lime and magnesia and iron and is readily attacked by basic slags. The fired Forsterite has only fair resistance to basic slags and is attacked by acidic slags. The field of oxide refractories has now been reduced to the alumina, magnesite, chrome classes. The magnesite is reported as having high refractoriness, high thermal conductivity, good resistance to basic slags, but poor resistance to slags containing high percentages of silica. Because of the latter, poor resistance to silica, magnesite and the combination of magnesite-chrome refractories do not appear desirable for use in a slagging gasifier. The use of a chrome refractory appears to be desirable; however, it is reported that under unusual conditions iron oxide is absorbed and causes a damaging expansion. High-purity alumina-type brick refractories have a high refractiveness with increasing alumina content, high mechanical strength at high temperature, and good resistance to most slags and fluxes. Therefore, the high-purity alumina refractories should be a good selection for a slagging gasifier. The alumina

brick are compatible with most of the other types of brick refractory. The combination alumina-chrome and magnesite-chrome-type bricks withstand slag erosion much better than alumina brick does,[5] and it appears that the alumina-chrome-type is the most acceptable.

In the classification of nonoxide refractories there are silicon carbide, carbon-graphite, boron carbide, and boron nitride. The common cause of failure for silicon carbide refractories is the oxidation of either the bonding material, silicon carbide, or both. These refractories have high thermal conductivity, high thermal shock resistance, high working temperature, high resistance to oxidation (except steam), excellent resistance to CO_2, CO, N_2, and high wear resistance.[13] The boron carbide and boron nitride refractories are specialty refractories.

In the selection of refractories, the thermal expansion may become an important consideration. The following approximate, reversible, thermal expansion of refractory brick can be anticipated at a temperature of approximately 2800°F.

Material (brick)	Linear expansion %
Silicon carbide	0.80
60%-70% Alumina	1.00
Silica	1.2
80%-90% Alumina	1.20
99% Alumina	1.35
92% Magnesite	2.0+

During thermal expansion the refractory brick is considered to be in compression and possess good strength. During thermal contraction (cool down) the refractory is considered to be in tension, thereby possessing poor strength. The refractory material will often fail if cooled suddenly from 2800°F.

The thermal conductivity of the following refractories may be important in the consideration of refractories. The following is a ranking of the various refractory brick as to their thermal conductivity which can be used as an indication of expected heat loss from the gasifier's "hot wall."

Material (brick)	Conductivity at 2800°F Btu/hr-ft^2-°F/in
60% Alumina	10
70% Alumina	12
Silica	14
90% Alumina (Korundal)	14
90% Alumina (Korundal XD)	19
99% Alumina	20
92% Magnesite	25
Silica carbide	40

IV. COMMERCIAL APPLICATION.

Known commercial applications of refractories in contact with slags are numerous. The blast furnace operations, the refractories used, and the various chemical actions that take place during operation of blast furnaces are discussed by Snow.[9] Some power generation plants have wet bottom (slagging) boilers in which refractories are required. In the processing of steel there is a need for refractories that will resist erosion of molten steel at 3000°F. In fact, the largest user of refractories is the steel industry.

In power generation station operations there are two basic types of wet bottom boiler: the pulverized coal unit (wet bottom) and the cyclone unit (wet bottom).[14] They basically operate at a high temperature, at atmospheric pressure, and with an oxidizing atmosphere. The walls of the combustion chambers in these furnaces are made up of studded, water-cooling tubes covered with refractory. Two refractory materials that are known to be used in cyclone and pulverized coal boilers are of the dense castable type; one, a phosphate-bonded 42% magnesia, and the other, a phosphate-bonded 93% alumina. Of the two, based on power-plant operations, alumina is preferred. Refractory in the cyclone boiler has a life of approximately 1 year for a thickness of approximately 1-1/2 inches. The life of the refractory in a pulverizing coal unit is approximately 2 years. The combustion reactants and gases are less erosive in a pulverized coal unit than in the cyclone boiler. It can be noted that the heat transfer differs, or the dense castable alumina with a thermal conductivity of approximately 10 Btu, in/hr, ft^2, °F is preferred over magnesite with a thermal conductivity 25.0 Btu, in/hr, ft^2, °F.

It was learned that power companies do have erosion/corrosion problems. They have accepted as routine the relining of their boilers every 1 or 2 years. Very few power plants are known to adjust their coal for slag fluidity. They experience "burn through" of the refractory and/or studs into their cooling tubes. When this happens they simply pump water through the tubes to make up for the loss of steam into the combustion chamber. If the burn through starts to get out of hand, the boiler is shut down for repairs and it is relined (1 to 2 years).

The steel industry has many uses for refractories. The following specific applications are of particular interest to the slagging gasifier design: (1) tap hole of an electric furnace, (2) pouring nozzle of the ladle, (3) tundish splash plate, and (4) the tundish nozzle. It was noted that the refractory material in these applications was fused refractory materials. Fused cast-magnesia is used in the tap hole of an electric furnace, and this block of magnesia lasts for approximately 1 month's operation. The pouring nozzle on the ladle was fused cast-alumina, the tundish splash plate was a densified 90% Al_2O_3 designated Korundal KD, and a block of cast Al_2O_3 that had been machined to size for the tundish nozzle. The ladle nozzle and tundish splash pad were used until replacement was necessary (approximately 25 heats). The tundish nozzle was replaced after every heat. None of the refractories in this particular steel mill were in contact with cooling coils.[15] Refractories in these applications realized large thermal stresses and very severe erosion conditions. In places where erosion is a prime concern, dense and nonporous refractories are often used. A discussion of "Erosion Behavior of Ceramics" was presented by S. M. Wiederhorn at the ERDA/MSF work shop (11/24-25/1975). Also, a paper entitled "Requirements for Ceramics in Coal Gasification Processes[5] which discusses the corrosive/erosion problems was presented by Mr. W. T. Bakker and Dr. M. S. Crowley. They emphasized the need to use dense refractories on the hot wall of the gasifiers (coal).

V. ERDA PILOT PLANTS.

ERDA is deeply involved in the construction and operation of several pilot plants, both nonslagging and slagging types. Of the nonslagging type, the Hy-gas and the Synthane pilot plants use a hard-face refractory on the hot wall backed up by an insulating-type refractory on the cold wall.[16,17] In the Hy-gas reactor, the internal lining (hot face) is "CASTOLAST G" (94% alumina, 5% lime). The same refractory is used as the working lining (hot face) in the Synthane plant. The working lining is backed up by an insulating lining of Harbison-Walker lightweight castable No. 28, 41% silica, 51% alumina in the Hy-gas plant, and Harbison-Walker "lightweight castable LI" (48% silica, 39% Al_2O_3, 11% lime) in the Synthane plant. All refractories contain a minimal of iron compounds to prevent carbon disintegration. The gas distribution plate in the Hy-gas gasifier is a special shape of "KORUNDAL XD".

There are three slagging gasifiers now being studied that are in the pilot-plant stage. They are Bi-gas, British Gas Slagging Lurgi in Westfield, Scotland, and the slagging, fixed-bed gasifier at Grand Fork, ND.

The refractories that were installed in the Bi-gas pilot plant were supplied by the Carborundum Company. The Bi-gas gasifier is built so that there are two combustion chambers. One chamber (stage I) oxidizes the char, forming slag and gases. The gas passes from this chamber (stage I) into the coal-gas entrainment chamber (stage II) where coal is reacted with the hot gases from stage I and produces synthetic natural gas and char. In stage I, the hearth and slag port is made of Monofrax A2 (99% A_2O_3), and the refractory is water-cooled. The wall and exit throat to stage I are formed by studded cooling tubes covered with refractory. The hot-wall material is Alfrax 96-F (97% Al_2O_3, 3% lime) which is a dense castable. This refractory material extends into stage II of the reactor. In stage II, the hot wall is composed of Alfrax 101 (99% Al_2O_3) a fused refractory, backed up by an insulating refractory wall. The insulating refractory is held in place by studded cooling tubes that form the cold wall of stage II. The insulating wall is composed of Alfrax B1-51 Bubble Al_2O_3, a hydraulic-setting castable (95% Al_2O_3, 4% lime). The refractory material used throughout the Bi-gas gasifier was material with no free iron (trace only), high alumina content (94% and up), and no silica (traces only). The hot-wall materials have good thermal properties such as low, hot-load deformation, low porosity, and a low thermal expansion; however, the material is somewhat susceptible to thermal shock. It was reported that the fused cast-Monofrax slag throat liner had cracked during startup of the reactor.[16] Basically, this was considered to be an operating problem, unique to the Bi-gas operations, which would be corrected by altering the startup procedure.

At the Grand Fork Energy Research Center, ND, ERDA has a slagging, fixed-bed gasifier. Refractory studies have been conducted in this gasifier. The refractory lining in the upper sections of the gasifier consists of a 2-11/16-inch inner layer of high-grade mullite tile with a service temperature of 3000°F. This tile is backed by 4-1/2 inches of insulating fire brick and 1-1/2 inches of insulating castable with a service temperature of 2800° and 2300°F, respectively. The slagging section of the furnace is made up of a 2-inch-thick, nitride-bonded silicon carbide refractory.[18] Special refractories were tested as insert rings for the tap hole through which slag exits the gasifier. These test rings were either self-bonded silicon carbide, titanium dioxide, hafnium carbide, or aluminum nitride. They reported that the silicon carbide had the best service life, which was about 30 to 50 hours of slagging operations.[19] The design of the tap hole was later modified by inserting a stainless steel cooling ring around the lip of the tap hole with the idea of utilizing frozen slag as a refractory. However, it was found that the slag tended to freeze and plug the tap hole at low slag

flow rates. In processing "Velva" lignite, the attack on the silicon carbide hearth was attributed to a high calcium content in the slag. In addition, the plugging of the tap hole was attributed to the slag being high in iron, thereby solidifying. Slag, high in iron, was reported to react with the silicon carbide. Thus, silica carbide and related nonoxide refractories do not appear promising. The use of cooling rings in direct contact with the molten slag would appear promising if a definite amount of slag flows over the ring so that a definite controlled cooling of slag can be accomplished. In practice, it is difficult to assure constant flow rates of slag because of the varying composition of the coals. This approach, water cooling the tap hole, seems to be a last resort.

VI. SUGGESTED REFRACTORIES.

A refractory system for a fixed-bed slagging coal gasifier is based on what is required of the material in the hostile environment of the gasifier and which materials are known to be available in the refractory industry. It has been assumed that water cooling a hot-face refractory within the gasifier is not the most desirable method because, unlike the design of boilers for producing steam, the purpose of a gasifier is to gasify coal, not make steam. The use of water to cool the hot-face refractory within a gasifier introduces a risk that the cooling tubes (or shell) could be penetrated, causing a rupture in the tubes, thereby, cooling down the refractory too rapidly and possibly causing a catastrophe by destroying the hot-face lining of the gasifier.

Another approach is the use of water-cooled coils in the slag port in an effort to build up a refractory layer of slag. This is an excellent idea except that it introduces a critical balance of heat flow to prevent either the fusing of slag and plugging the slag tap hole or because of over heating, causing the burn-through of the water-cooled coils and the loss of an operating gasifier. Finding a refractory material that will withstand the hostile conditions – an ideal refractory material, appears to be the most feasible answer.

The refractory industry does not have the ideal refractory, although they claim to have refractory materials that will satisfy the operations of either a slagging or nonslagging coal gasifier. Today there is a technology for constructing a slagging or nonslagging gasifier without the use of water-cooling coils and using a refractory material with a life span of 1 to 2 years. Harbison-Walker Refractories recommend the use of solid solution bonded Al_2O_3 - Cr_2O_3 refractory (Ruby Brick) for slag resistance (tap hole and hearth areas).[16,20]

The Harbison-Walker Refractories densified alumina-chromic oxide-plastic brick has good properties when compared to mullite-bonded 72% alumina, mullite-bonded 90%, and sintered 99% alumina in tests using acidic slags by the drip and impingement tests. The three types of slags were used in these tests and they had a basicity range,

$$\text{basicity} = \frac{CaO+MgO}{Al_2O_3+SiO_2}$$

from 0.61% to 1.17% and an iron content range from 0.6% to 22.7%.[21] This type of Al_2O_3 - Cr_2O_3 brick is presently being tested and evaluated at Pittsburgh Energy Research Center (PERC). The Al_2O_3 - Cr_2O_3 brick along with a plastic Al_2O_3 - Cr_2O_3 are good candidate materials for use in the slag zone of a slagging, fixed-bed coal gasifer. This material could be used to form the slag tap hole and the hearth and side wall of the high temperature reaction zone (2600° to 3000°F). Behind this hot wall, a compatible insulating refractory material such as bubble

alumina with high temperature insensitivity should be used. Away from the highly reactive zone of the gasifier and with the thought of reducing costs, the relatively impervious hot wall could be a type brick composed of 90% Al_2O_3–10% SiO_2, and the upper zone of 70% Al_2O_3–30% SiO_2 brick followed by a monolithic-type 40% to 60% Al_2O_3 refractory. All hot-wall refractories should be dense, very low porosity, and of a low iron material.

Again, it is recommended that a compatible insulating refractory material be used to insulate the hot wall instead of water cooled tubes. This is recommended to prevent catastrophic failure of the gasifier resulting from a break-out of the water-cooled tubes. Dr. Roy E. Dial[22] in his article suggested the following thermal profiles of refractory lining, table 4 and figure, for furnaces not utilizing water-cooling tubes to cool the "hot-wall" refractory.

Table 4. Thermal Profiles of Refractory Linings

HOT FACE °F	INTERFACE °F	INTERFACE °F	COLD FACE °F	HEAT LOSS BTU
DENSE ALUMINA CASTABLE (4") + BUBBLE ALUMINA CASTABLE (6")				
1900	1588	–	400	1989
2600	2159	–	475	1543
2900	2403	–	504	1740
3200	2646	–	531	1931
DENSE ALUMINA SHAPE (4.5") + BUBBLE ALUMINA SHAPE (4.5") + K-28 INSULATING BRICK (4.5")				
2600	2452	1958	347	824
2900	2728	2156	373	953
3200	3005	2353	399	1086

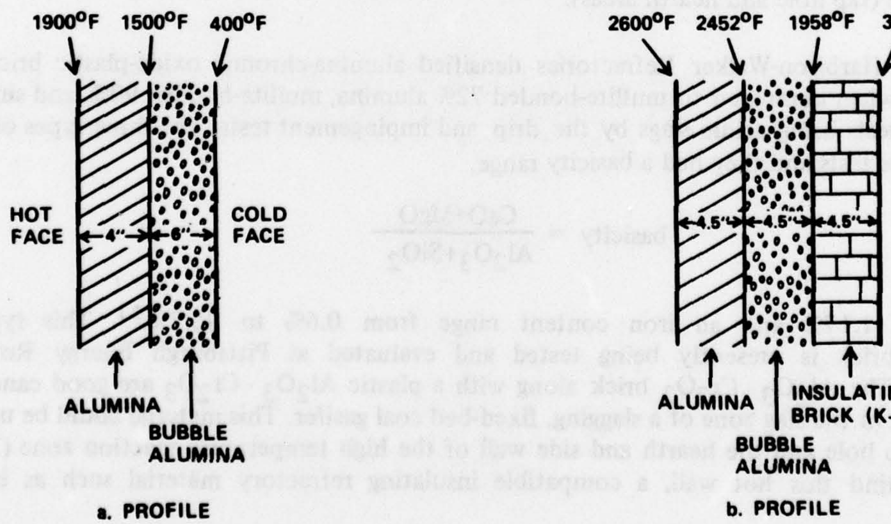

Figure. Thermal Profiles of Refractory Linings (from table 4)

VII. CONCLUSIONS.

It is concluded that:

1. Water cooling the hot-face refractory wall in a gasifier should be avoided, if possible.

2. Water cooling the tap hole for the purpose of forming a refractory slag is difficult to control and should be avoided, if possible.

3. Technology exists to design and construct a gasifier without water cooling the hot wall and slag tap hole of the gasifier. (This should be verified by pilot-plant testing.)

4. Hot-wall refractories should be dense, low porosity, and contain no active iron.

5. In the hot-slag forming zone of the gasifier, the densified alumina-chromic oxide brick should be utilized.

6. A compatible refractory insulating material such as "bubble" alumina should be used to backup the hot wall of the gasifier.

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